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IN-SITU CLAY FORMATION:
A NEW TECHNOLOGY FOR STABLE CONTAINMENT BARRIERS

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Containment of chemical wastes in near-surface and repository environments is accomplished by designing engineered barriers to fluid flow. Impermeable barriers are intended to contain wastes for subsequent cleanup treatment or for longer-term isolation in cases where no effective cleanup treatment yet exists. Impermeable barriers also have recently been applied as components of "funnel and gate" approaches to selectively channel contaminated fluid flow through a reactive treatment zone. Containment barrier technologies such as clay liners, soil/bentonite slurry walls, soil/plastic walls, artificially grouted sediments and soils, and colloidal gelling materials are intended to stop fluid transport and prevent plume migration. However, despite their effectiveness in the short-term, all of these barriers will exhibit geochemical or geomechanical instability over the long-term resulting in degradation of the barrier and its ability to contain waste.

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PROJECT BACKGROUND

Containment of chemical wastes in near-surface and repository environments is accomplished by designing engineered barriers to fluid flow. Impermeable barriers are intended to contain wastes for subsequent cleanup treatment or for longer-term isolation in cases where no effective cleanup treatment yet exists. Impermeable barriers also have recently been applied as components of "funnel and gate" approaches to selectively channel contaminated fluid flow through a reactive treatment zone (Shoemaker et al., 1996). Containment barrier technologies such as clay liners, soil/bentonite slurry walls, soil/plastic walls, artificially grouted sediments and soils, and colloidal gelling materials are intended to stop fluid transport and prevent plume migration. However, despite their effectiveness in the short-term, all of these barriers will exhibit geochemical or geomechanical instability over the long-term resulting in degradation of the barrier and its ability to contain waste. For example, grouts and colloidal silica both require saturated conditions to maintain their structural integrity (Rumer and Ryan, 1995; Whang, 1996).

A new type of containment barrier with a potentially broader range of environmental stability and longevity could result in significant cost-savings to the DoD and DOE. In this project, we plan to precipitate clays *in-situ* in porous geologic materials by building on the technologies that exist for colloidal or gel stabilization. Unlike colloidal or gel barriers, however, a precipitated-clay barrier does not require saturated conditions to be functional. Thus, it can be emplaced without loss of performance in the vadose zone as well as areas with fluctuating water tables. Clays have the advantage of being geologically compatible with the near-surface environment, and naturally sorptive for a range of contaminants. The precipitation of clays in-situ in soils and sediments should result in reduced permeability and hydraulic conductivity, and increased mechanical stability through cementation of soil particles. By analogy with natural diagenesis in sedimentary rocks, we intend to engineer "artificial" lithification in soils and sediments. Unlike natural diagenesis, however, the time-scale for clay growth will be accelerated greatly from more than tens of thousands of years down to a few weeks.

Currently, 17,000 DoD sites are undergoing remediation at a cost of $35 billion. Projected costs of site cleanup at current and former DoD and DOE sites are $200 billion. Advantages of our proposed technology for a new stable containment barrier will lead to reduced costs, reduced risk to the environment and human health, and increased safety of site cleanup. Specific advantages include (1) providing containment thereby allowing time to perform in-situ treatment of waste, (2) a method for forming a barrier directly beneath a contaminated site, (3) a decrease in the number of containment walls or repairs to containment walls needed over the lifetime of a contaminated site, (4) a method for stabilizing contaminated soils and sediments, and (5) a containment barrier appropriate for arid as well as humid environments, and for saturated, unsaturated, or fluctuating water table conditions.

OBJECTIVE

We plan to (1) confirm published results suggesting that clays can be precipitated in a few weeks to months from aqueous gels; (2) design an optimal gel composition that will

maximize clay yield and crystallization rate, while maintaining injectability in soils and sediments; (3) test the barrier formulation in the laboratory; and (4) test the method in a field experiment.

This project will be carried out over four years. The first two years will be spent developing the method in the laboratory. In this effort, our objective is threefold. We intend to (1) assess published results showing that clays can be precipitated in a matter of a few weeks to a few months from an aqueous gels, (2) design an optimal composition of aqueous gel solution for maximum clay yield and crystallization rate, while maintaining injectability into porous soils and sediments, and (3) test the method in sandbox or column experiments in the laboratory. Various analyses will be conducted of the synthesized clays and clay materials in order to determine composition and crystallinity; particle size and shape; and location of clay growth sites within a sediment. The critical key step in developing the new barrier technology will be to successfully optimize the formation of clays from aqueous gels under ambient conditions.

Success of the method will be demonstrated in laboratory tests on quartz sands and natural soils or sediments by obtaining a significant reduction in permeability (or hydraulic conductivity) and increase in geomechanical stability. Once success is demonstrated in the laboratory, we plan to test the methodology at an appropriate NETTS test site. Field testing would take place in the project's third and/or fourth years. Field testing would likely continue in conjunction with laboratory work focused on a specific chemical and geological system.

TECHNICAL APPROACH

The technical approach is multidisciplinary involving principal investigators with expertise in geochemistry, mineralogy, geophysics, hydrogeology, and environmental engineering. Each research stage will employ the principal investigators to varying extents.

The first stage of our research is being focused on synthesizing clays and claylike materials in the laboratory at room or ambient temperature. Researchers at the University of Colorado and the University of Wisconsin are the primary investigators for this work. The approach has been to reproduce experimental designs from a number of published studies in which clay products were identified (e.g., Decarreau 1980, 1981; Decarreau and Bonnin, 1986; Decarreau et al., 1987; Flehmig, 1992; Harder, 1971, 1974, 1976, 1977, 1978; Hem and Lind, 1974; La Iglesia Fernandez and Martin Vivaldi, 1973; La Iglesia and Martin-Vivaldi, 1975; La Iglesia and Serna, 1974, Linares and Huertas 1971a,b; Siffert, 1962; Siffert and Wey, 1973). We have also synthesized an anionic clay called a layered double hydroxide (Cavani et al., 1991) which has a naturally occurring mineral counterpart called a hydrotalcite (e.g., Taylor and McKenzie, 1980). A third type of material we are investigating falls within the new class of mesoporous silica materials that can be formed at room temperature using surfactant templates (e.g., Kresge et al., 1992; Anderson et al., 1995; McMullen et al., 1995). A related study with researchers at the University of Grenoble was conducted to investigate the nucleation of clays on quartz surfaces under ambient conditions (Manceau et al., submitted).

Synthesis of clays is the critical key step in developing the new barrier technology. Aqueous solutions and/or low viscosity gels are composed using recipes taken from the literature involving reactions and additives known to promote clay formation. Characterization of the clay with respect to quantity, composition, and crystallinity is being conducted using a variety of analytical techniques. These include powder X-ray diffraction (XRD) for phase identification and atomic force microscopy (AFM) for particle size and shape. Solution compositions from which clays form are being measured to assess the saturation states of the solutions needed for clay nucleation and growth as well as equilibrium solubilities of the synthesized solids. The actual clay synthesis experiments and these three analyses are being carried out at the University of Colorado. Transmission and analytical electron microscopic analyses is being carried out at the University of Wisconsin. With these data, we can fully assess the solid phases produced in any experiment and obtain a measure of quantification of the clay yield and crystallinity.

The second step is to form the solids in-situ in quartz sediments or natural sediments in the laboratory. Emplacement of the solutions/gels in the laboratory tests will emulate field technologies such as permeation and jet grouting, and soil-mixing. Characterization of the "in situ" precipitated clays will be made by measuring gas permeability, hydraulic conductivity, freeze/thaw stability, and mechanical strength. We will also characterize the porosity distribution after precipitation of the clays using laser confocal scanning microscopy (Fredrich et al., 1995). Laser confocal scanning microscopy will give us a three-dimensional image of the sediment plus precipitated clay from which we can determine information about nucleation sites and porosity connectivity. This work will be carried out between researchers at the Universities of Colorado and Wisconsin and investigators at Sandia National Laboratories. Nearly all barrier material tests will be conducted at Sandia.

A key decision point will be made at the end of the second year of research. We must demonstrate that: (1) practical quantities of clays can be formed; and (2) when clays are precipitated in situ in soils or sediments in the laboratory, the material properties are improved over those of existing containment barriers.

Upon successful completion of the second year of work, we will begin to test the methodology in a field experiment. This could take place at the NETTS Dover Test Site (formerly known as the Groundwater Remediation Field Laboratory) at Dover Air Force Base. Alternatively, or in addition to an eastern humid site below the water table, we would like to demonstrate the methodology in an arid environment under unsaturated groundwater conditions. The small-scale field experiment will primarily assess the technology's success under ambient conditions and at a scale representative of ultimate application. Stability and flow properties of the field-emplaced material will be measured both from a laboratory perspective using small samples taken from the field, and from on-site field testing where practicable.

PROJECT ACCOMPLISHMENTS

During the first seven months of the project (begun late due to funding delays), we investigated various methods of precipitating clays and claylike materials under ambient conditions. We have successfully formed clay (kaolinite), layered double hydroxide (Li/Al

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nitrate), and mesoporous silica/alumina materials in one to six weeks at 22°C. In other clay-synthesis experiments we were not successful, particularly the synthesis of illite in the presence of kaolinite and KOH solutions. Also, we are also still working on perfecting the reproducibility of the kaolinite synthesis method. We have also shown in collaboration with researchers in the Environmental Geochemistry Group at the University of Grenoble that trioctahedral clays nucleate in the surfaces of quartz grains within six days at 22°C.

We have tested the ability of the mesoporous silica/alumina materials to sorb dissolved organics from aqueous solutions which to our knowledge is a new application of these new materials. We have also selected two model sediments for our initial laboratory in situ synthesis experiments.

Details of the progress status in each of these subject areas are listed below.

I.   Synthesis of kaolinite at room temperature

Introduction: Kaolinite ($Al_2Si_2O_5(OH)_4$) is a nonexpandable clay that forms naturally in humid weathering environments during the weathering of igneous rocks, usually from feldspar minerals. Most attempts to synthesize kaolinite at room temperature have been unsuccessful due to the slow kinetics of the process (e.g., Kittrick, 1970). In fact, it is virtually impossible to reverse solubility measurements of kaolinite at 25°C because rates of dissolution and precipitation are extremely slow near equilibrium. Equilibrium has never been approached successfully with respect to kaolinite from purely inorganic supersaturated solutions at 25°C.

The only systems in which kaolinite synthesis has been reported at room temperature have included various organic components thought to accelerate the reaction through either a templating or complexation effect (Linares and Huertas, 1971a,b; Siffert and Wey, 1973; La Iglesia Fernandez and Martin Vivaldi, 1973) on the Al-octahedral sheet. Therefore, we have chosen this approach and performed similar experiments with promising results.

Methods: A fulvic acid solution containing 600 ppm C was prepared in deionized water. (All experiments described in this report used Barnstead UV-deionized 18 MΩ-cm water and reagent grade chemicals purchased from Fisher Scientific, Aldrich, or Sigma). The fulvic acid was Suwannee River Fulvic Acid Standard, denoted as SFA, obtained from the International Humic Substances Society (IHSS). Stock solutions were prepared of 1000 ppm Al (from $AlCl_3$ using deionized water, pH ~ 3) and 1000 ppm Si (from $Na_2Si_2O_3 \cdot 9H_2O$ using deionized water, pH > 10). All experimental solutions were made from these three stock solutions.

The first experiment was conducted as followed. One mL of fulvic acid solution was pipetted into a 50 mL plastic test-tube. To this was added 1.537 mL of the Al stock solution. The two solutions were mixed by shaking for about 2 mins, following which 1.6 mL of the Si stock solution was added. The solution volume was increased to 40.0 mL by adding 36.86 mL deionized water and its pH was adjusted to around 9 to 10 (measured with pH test paper) using 1 N NaOH and/or 5 N HCl. No precipitate was observed after a few minutes. So, addition of the same amounts of the Al and Si stock solutions was repeated and the solution pH was readjusted to the 9-10 range, bringing the final volume to about 43.4 mL. Immediately, a cloudy brown precipitate was observed. The experiment was held at room temperature for 42 days during which the test-tube was shaken occasionally. After 19 days, about 1 mL of the precipitate was

extracted and air-dried at room temperature for XRD analysis. No crystalline peaks were observed. After 42 days the precipitate was recovered by centrifugation and washed once with deionized water. The final pH value of the solution was 9.13 as measured using a glass electrode. The final Si, Al, and C concentrations of the solution were not measured. The precipitate obtained after centrifugation was dropped onto a glass slide and air-dried.

The final precipitate was analyzed by powder XRD using a Cu-Kα source. Grain size and shape were measured using a Digital Instruments (DI) Nanoscope IIIa Multimode Atomic Force Microscope (AFM) in TappingMode with silicon tips (DI). Kaolinite was also identified by electron dispersive spectrometry (EDS) and selected area electron diffraction (SAED).

Thirty-eight experiments have been run or initiated to duplicate the results obtained from the first experiment. Of these, thirty-four were conducted using Suwannee River Fulvic Acid and various Al and Si concentrations, as well as initial and final pHs. Two were run using IHSS Peat Fulvic Acid Standard and two were run using IHSS Suwannee River Humic Acid Standard. Analyses of the run products are ongoing and will be reported on as they are obtained. Complete analyses of all solutions (Si, Al, C, and pH) are also being carried out. Si and Al concentrations are determined by UV-visible light spectrophotometry using a Bausch and Lomb Spectronic 501 UV-visible light spectrophotometer and the complexation methods of Dougan and Wilson (1974) for Al and Koroleff (1983) for Si. Dissolved C will be determined using a Total Organic Carbon (TOC) analyzer. Solution pH is measured by electrode using standard NIST pH buffers.

Results and Discussion: In the first experiment, sharp kaolinite XRD peaks were observed in the run product (Figure 1), indicating that the product had good crystallinity. The X-ray data are
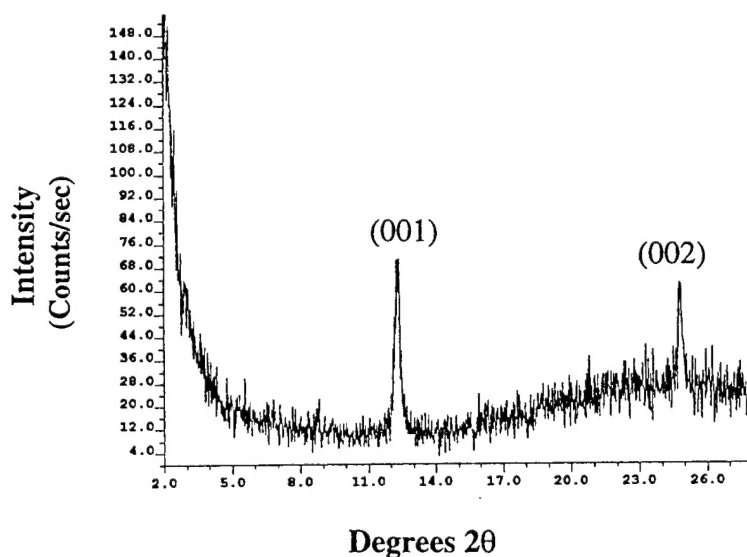

Degrees 2θ

Figure 1: Powder XRD pattern of synthesized kaolinite from experiment KSFA1. The (001) and (002) peaks are sharp and narrow indicating good crystallinity. The low intensity and absence of distinguishable higher order peaks indicates that the quantity of product is low. The d-spacing for the (001) peak is 7.155 Å, matching exactly that for published XRD patterns for kaolinite.

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supported by the crystal size and shape images obtained using AFM (Figure 2a). The AFM data indicate that kaolinite particles are on the order of 0.1 to 0.2 microns in diameter, hexagonal in shape, and platy. These are characteristics of natural kaolinites as shown in Figure 2b. SAED and Energy Dispersive Spectroscopic (EDS) analyses also indicate that the run product contains kaolinite. The SAED analyses show a second particle with a Na-Si gel composition, which is consistent with the aqueous solutions used in the experiment. These particles are likely the less crystalline smaller particles shown in Figure 2a.

Thus, the results of this experiment confirmed that fulvic acid can catalyze kaolinite formation at room temperature based on the published work of Linares and Huertas (1971a,b) and of La Iglesia Fernandez and Vivaldi (1973). Based on preliminary visual observations, 21 of the 24 experiments using Suwannee River Fulvic Acid, both experiments using Peat Fulvic Acid, and one of the experiments using Suwannee River Humic Acid have all yielded precipitates similar to those initially observed in the first successful experiment. Final run products taken from four of the 38 additional experiments have been sent for TEM/SAED analyses. The remaining 34 experiments are still running. These products were separated in a slightly different way for TEM analysis. First the slurries were centrifuged and the supernatant decanted. Then the remaining slurry was washed with deionized water and filtered through a 0.2 micron cellulose filter paper. We are waiting for the results back from the University of Wisconsin.

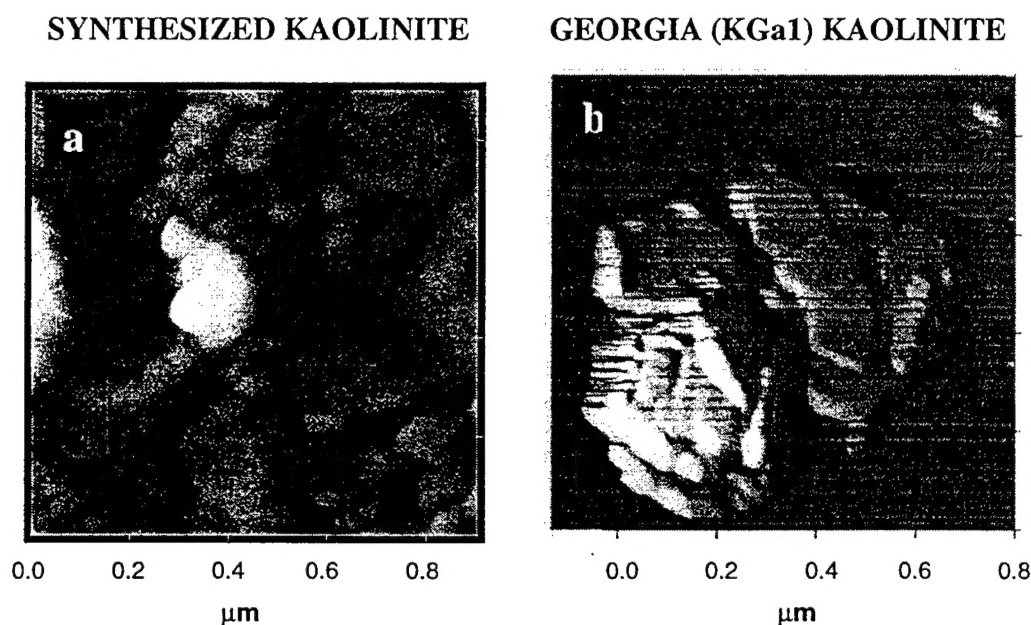**SYNTHESIZED KAOLINITE**   **GEORGIA (KGa1) KAOLINITE**

Figure 2: Comparison of Atomic Force Microscopy images of synthesized kaolinite (left) and a kaolinite standard (KGa1 from the Clay Minerals Society Source Clays Repository). The synthesized kaolinite contains two types of particles: hexagonal plates and smaller rounded grains. The hexagonal plates are of approximately the same size and shape as the smaller particle in the figure on the right.

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Once we have demonstrated that we can reproduce the production of kaolinite (which is fully expected based on the published data showing that kaolinite can be precipitated from Al and Si-bearing fulvic acid solutions over a range of pH from 3 to 8), we plan to systematically evaluate how to optimize the yield. Yield optimization may be accomplished by adjusting the initial supersaturation state of the solution (e.g., Al and Si concentrations, pH) and/or by optimizing the fulvic acid in some way. We have obtained fulvic acid from other sources (peat and Nordic soil, International Humic Substances Society), and will investigate their effectiveness in forming kaolinite. We are also investigating the possibility and cost of synthesizing fulvic acid using published methods for humic acid synthesis (e.g., Ladd and Butler, 1966; Mathur and Schnitzer, 1978). In these methods humic acids precipitate from solution leaving fulvic acids (that are water soluble due primarily to their smaller molecular size) in solution.

II. Room-Temperature Synthesis and Characterization of Li/Al Layered Double Hydroxide (Li/Al LDH) [LiAl$_2$(OH)$_6$]NO$_3$•nH$_2$O

Introduction: Layered double hydroxides (LDHs) are an important type of material being investigated by many researchers for their catalytic and sorbing properties (Cavani et al., 1993). They can be described as antitypes of 2/1 clay minerals (three-layered clay minerals) and consist of positively charged metal oxide/hydroxide sheets with intercalated anions and water molecules. The oxide sheets contain excess positive charge which is balanced by the interlayer anions. In this way LDHs can act as sorbents for anionic contaminants. LDHs are reported to be easily synthesized at low temperature and pressure (e.g., Schwertmann and Fechter, 1994; and certain compositions are found in nature (e.g., Taylor and McKenzie, 1980). In this part of the project we are examining the synthesis and stability of selected LDH compounds under ambient conditions for use as an in-situ precipitate.

Methods: Li/Al nitrate LDH was synthesized using a method similar to that described by Meyn et al. (1993). Aluminum hydroxide was precipitated by addition of a NaOH solution (about 2 M) to a solution of 20 g of Al(NO$_3$)$_3$•9H$_2$O (0.053 m) in 225 mL of water. Then 17 g of LiNO$_3$ (0.25 m) in 50 ml of water was added while stirring. The dispersion was held at room temperature for 25 days with occasional shaking. The precipitate was washed until the solution pH approached ~ 7 and dried at 65°C.

Results and Discussion: The resulting product was characterized by XRD (Figure 3). We are currently resynthesizing this particular LDH and drying the sample at room temperature. Next we plan to determine the solubility of the material in water over the pH range 4 to 8. Other LDHs containing Ca and/or Mg as the primary divalent cation, and chloride or sulfate as the anions will be tested.

Synthesis of Al-bearing LDHs in the presence of silicate minerals typically found in a soil or sediment in and of itself is not expected to be a problem. Their solubility is also expected to be a minimum near neutral pHs similar to the solubility of Al-hydroxide minerals such as gibbsite. However, an important question is will the LDHs nucleate on the silicate mineral grains in such a way as to truly cement the grains together? In order to do so it is likely that the hydroxide sheets of the LDHs will need to combine with repolymerized silica tetrahedral sheets
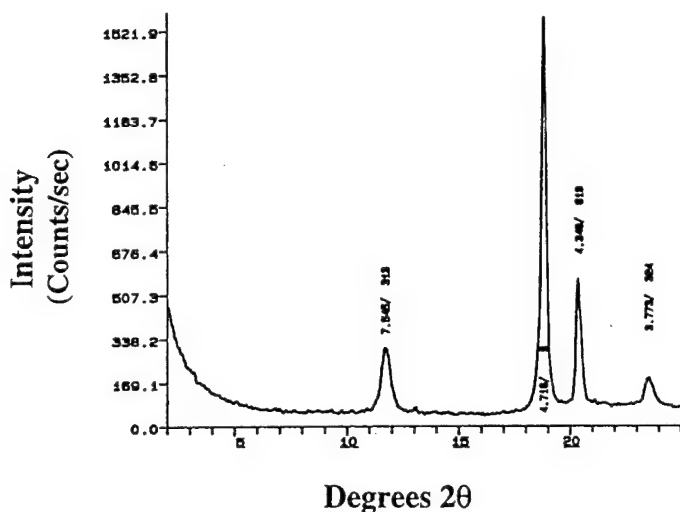
Figure 3: Powder XRD pattern of Li/Al LDH.

that may form in the surfaces of quartz grains (see section VI below) to form 2:1 layer clays. We will pursue this hypothesis in the coming months.

II.   Room-Temperature Synthesis of Surfactant-Templated Mesoporous Materials

Introduction: Researchers from Mobil Oil Corporation discovered a new family of ordered mesoporous silica materials, designated M41S, in 1992 (Kresge et al., 1992; McCullen et al., 1995). These materials may contain pore sizes ranging from < 13 to 100 Å (Monnier et al., 1993) which can be controlled using a liquid crystal templating mechanism. In this mechanism, surfactant molecules determine the actual structure and pore sizes of the solids. The materials may be synthesized at both ambient (Anderson et al., 1995; Voegtlin et al., 1997) and higher temperatures. Al may also be added to make a mesoporous aluminosilicate (Beck et al., 1992; Chen et al., 1993). For catalytic applications, the solids are calcined to remove the surfactant template and leave a high surface area porous solid.

MCM-41 calcined materials have shown great affinity for sorbing benzene from the vapor phase (Beck et al., 1992; McCullen et al., 1995). This sorbent behavior of the pure-silica MCM-41 samples suggests that they are potential sorbents for large organic pollutants from waste or drinking waters (Tanev and Pinnavaia, 1995). However, to our best knowledge, no studies have been conducted yet on the use of mesoporous silicates for removing organic pollutants from water. As synthesized, i.e., without removing the surfactants, these surfactant-templated mesoporous materials may have unique sorptive properties for hydrophobic organic compounds in water as compared to organic-derived-clays (i.e., organic-cation-exchanged clay minerals (Boyd et al., 1991)).

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The composition (silicate or aluminosilicate), sorptive potential for organics, and room-temperature synthesis of the M41S materials suggest that they may be useful materials for in-situ precipitation to develop containment barriers. Therefore, in this project we are pursuing their synthesis at room-temperature, stability in aqueous solutions, and ability to sorb organic waste contaminants (see Section IV, for preliminary results on the latter topic).

Method for Synthesis of Pure-Silica MCM-41: Pure silica MCM-41 was synthesized according to a room-temperature procedure described by Anderson et al. (1995). Deionized water (13.64 g) and methanol (4.90 g) were combined with 0.13 mL of 50 wt % aqueous NaOH solution (1.14 x 10^{-3} m) resulting in a solution with a pH of 12.7. Subsequently, 1.408 g of cetyltrimethylammonium bromide (C_{16}TABr) and 1.25 mL of tetramethyl orthosilicate (TMOS, 8.47 x 10^{-3} m) were added under stirring. The final molar ratio was TMOS:C_{16}TABr:H_2O:MeOH = 1.0:13:97:18. A thick milky suspension formed within a minute, which was further stirred for 15 min and left at room temperature for 24 hrs. Filtration was followed by prolonged washing with water until no surfactant bubbles were produced. The samples were then dried at 70°C.

Method for Synthesis of Aluminosilicate MCM-41 (with Si/Al = 15, 20, 30, 40): Si/Al MCM-41 was synthesized by following a modified room-temperature procedure described by Anderson et al. (1995). A mixture of deionized water (7.35 g containing desired amount of $AlCl_3$) and methanol 2.45 g was adjusted quickly with 50 wt % aqueous NaOH solution to result in a solution with a pH of 12.7. Subsequently, 0.2 g of cetyltrimethylammonium bromide (C_{16}TABr) and 0.625 mL of tetramethyl orthosilicate (TMOS, 4.19 x 10^{-3} m) were added under stirring. A thick milky suspension formed within 2 min, which was further stirred for 30 min and left at room temperature for 48 hrs. Filtration was followed by prolonged washing with water until surfactant bubbles no longer formed. The sample then was dried at 70°C.

Results and Discussion: The surfactant-templated mesoporous materials can be easily synthesized at ambient conditions as reported in the literature. Representative XRD patterns are shown in Figures 4 and 5. Although we have washed the materials in the initial synthesis work for their characterization, it would not be necessary to do so for in situ precipitation. Excess surfactant would likely sorb to other grains. In fact, it is possible that "excess" surfactant would do exactly that and in such a way bind the precipitated mesoporous silicates to the soil mineral grains directly.

In the near future we intend to optimize the synthesis by using inorganic (rather than organic) sources of Si (such as Na-silicate) and Al. This will reduce potential contamination problems during in situ precipitation. We have also started a series of solubility experiments on the pure Si and Si/Al materials to determine their stability in pH 4 to 8 solutions.
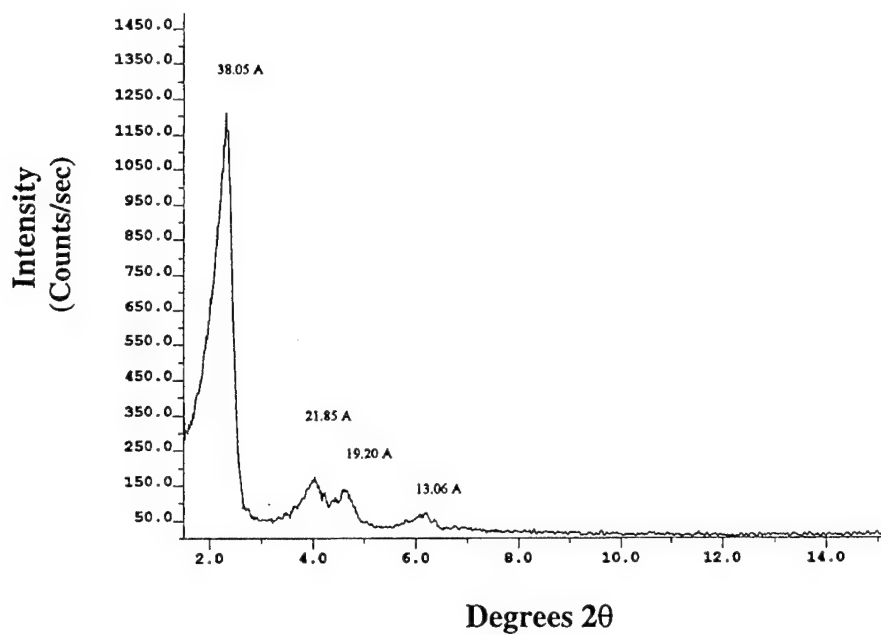
Figure 4: Powder XRD pattern of synthesized MCM-41 (pure Si). D-spacings are given above the peaks in units of Angstroms.
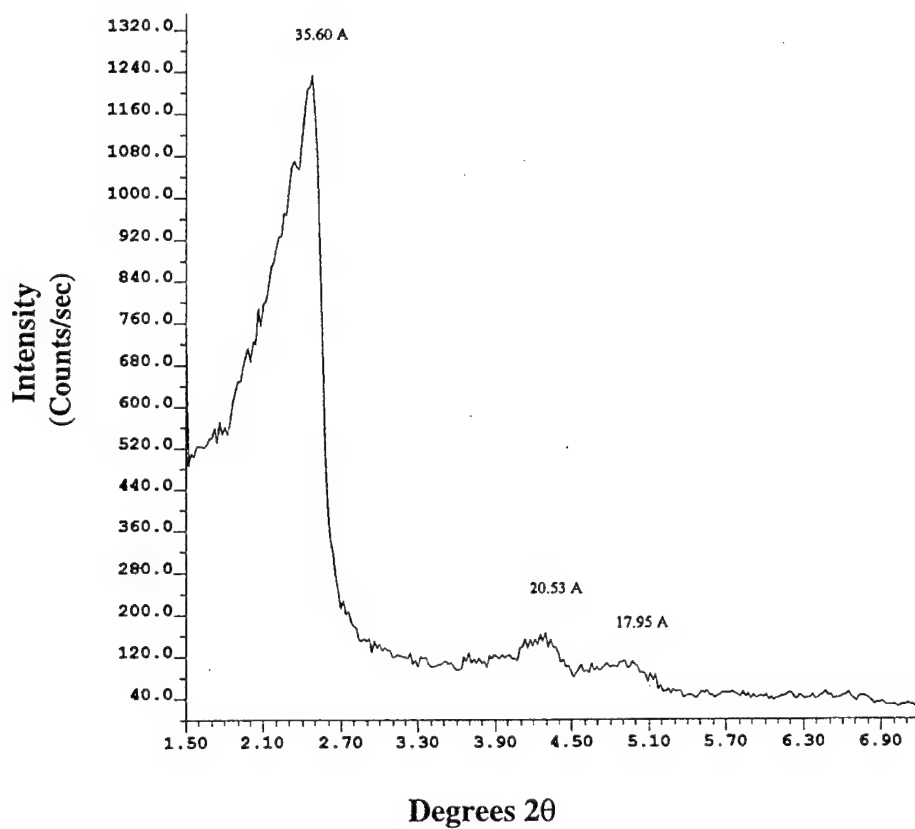

Figure 5: Powder XRD pattern of synthesized MCM-41 (Si/Al = 40). D-spacings are given above the peaks in units of Angstroms.

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III. Examination of Sorption Behavior of Mesoporous Silicate Materials for Organics

Introduction: As stated in Section III, mesoporous silicate materials have great potential for sorbing organic contaminants directly from water. Therefore, we conducted a series of sorption experiments at room temperature using a suite of the noncalcined materials and the organic substances benzene, toluene, m-xylene, trichloroethylene, tetrachloroethylene, and 1,2,3-trichlorobenzene.

Methods: Batch sorption isotherms were determined by weighing 100 mg samples of pure Si, and the aluminosilicate materials with Si/Al = 20, 30, 40 into 25 mL Corex glass centrifuge tubes that contained 25-28 mL distilled water. Reagent grade organic compounds (Aldrich, 99+ %) were added using a Hamilton microliter syringe either as the neat liquid or as a methanol-based stock solution. The concentration of organic compounds did not exceed their water solubility. After appropriate volumes of the chemicals were added, the centrifuge tubes were immediately closed with foil-lined screw caps and shaken for 24 hrs on a reciprocating shaker at ambient temperature ($25 \pm 1°C$). Based on similar experiments with organo-clays and organo-intercalated LDHs, the experimental duration of 24 hours is probably sufficient to achieve equilibrium sorption. However, confirmation that the remaining solution concentrations are equal to the equilibrium concentrations remain to be shown. After centrifugation, a 10 mL aliquot of the supernatant liquid was extracted in a septum-capped, 20-mL vial with 10 mL of hexane (for trichloroethylene, tetrachloroethylene and 1,2,3-trichlorobenzene) or 10 mL of carbon disulfide (for benzene, toluene and *m*-xylene). A portion of the hexane or carbon disulfide containing the extracted chemicals was analyzed using gas chromatography (Zhao and Vance, 1998). Isotherms were constructed by plotting the amounts sorbed versus the concentrations remaining in solution. The average blank recoveries were high (> 93%) and the data were not adjusted for these recoveries. (Some of the organics are lost from the experimental systems due to their volatility.)

Results and Discussion: Representative results are shown in Figure 6 for sorption of tetrachlorethylene on the materials. Data for all organics investigated are being reduced now. It is clear from the preliminary data analyses, however, that the as-synthesized MCM-41 materials have very strong affinities for the organic pollutants studied. In fact these sorption affinities are comparable to those demonstrated by organo-LDHs (Zhao and Vance, 1998). This suggests that in-situ formation of clay-like MCM-41s as barrier materials for immobilizing organic pollutants may be a promising remediation technology. A manuscript is in preparation for publication on the sorption results. The working title and authorship are "Exploration of Mesoporous Silicate Materials for Immobilizing Organic Waste Contaminants in Groundwater Systems" by H. Zhao, K. L. Nagy, and G. Vance.
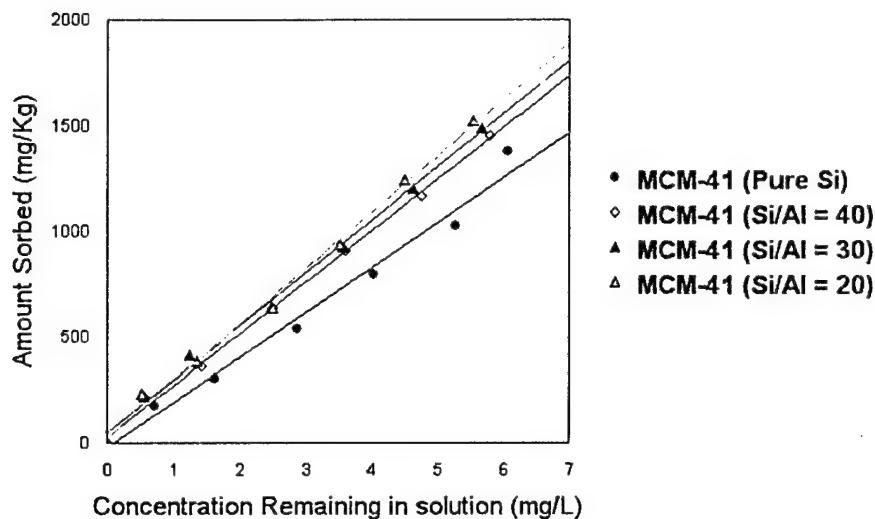
Figure 6: Sorption isotherms for tetrachloroethylene on MCM-41 mesoporous silicates and aluminosilicates. The amount sorbed is in units of mg tetrachloroethylene per kg of the solid and is plotted vs. the concentration remaining in solution in units of mg per L of solution.

V.   Transformation of Kaolinite to Form Illite

Introduction: Bauer (1997) reported forming fibrous illite from kaolinite in alkaline solutions at room and lower temperatures in a few days (pers. comm.) to months. In these experiments the kaolinite is the source of Si and Al for the illite, and a KOH solution is the source of K. We performed a series of experiments to reproduce Bauer's results with the idea that illite ($KAl_3Si_3O_{10}(OH)_2$) could be induced to nucleate on quartz grains under the alkaline conditions during in-situ synthesis. If this could be made to work, the process would simulate the great reduction observed in porosity and permeability by growth of illite in sandstones during burial diagenesis in sedimentary basins (e.g., Pallat et al., 1984; Kantorowicz, 1990, Kantorowicz et al., 1992). This section of the report describes the experiments performed thus far. We have not been successful yet at forming illite using this approach. However, we may revisit this method after an in-person meeting with Bauer at a conference in Karlsruhe in March, 1999.

Methods: Well-crystalline kaolinite (KGa-1b) and poorly crystalline kaolinite (KGa-2) standards were obtained from the Clay Minerals Society Source Clays Repository and used as starting materials in the experiments. Six experiments were performed in which kaolinite was added to KOH or KOH + KNO_3 solutions (Table 1). Reagent grade chemicals and deionized water were used in all experiments. These preliminary experiments were run at 65°C in sealed bottles in an oven to accelerate the reaction according to the results of Bauer (1997). The bottles were shaken by hand periodically. After 15 days, a portion of the suspension from each experiment was centrifuged, washed once with deionized water and analyzed by XRD.

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TABLE 1: Details of and results for kaolinite to illite transformation experiments.

Experiment Number	Kaolinite	KOH(aq)	KNO_3(aq)	XRD results
a	KGa-1b	80 mL of 0.5 M	80 mL 0.5 M	kaolinite
b	KGa-2	80 mL of 0.5 M	80 mL 0.5 M	kaolinite
c	KGa-1b	80 mL of 3.0 M	0	zeolite + feldspar
d	KGa-2	80 mL of 3.0 M	0	zeolite + feldspar
e	KGa-1b	80 mL of 0.5 M	0	kaolinite
f	KGa-2	80 mL of 0.5 M	0	kaolinite

Results and Discussion: XRD results showed no change from the original kaolinite diffraction pattern for experiments (a), (b), (e) and (f). We did observe zeolite, possibly feldspar and some kind of unidentified mica, and the nearly complete absence of kaolinite peaks in experiments (c) and (d) (Figure 7). Based on these initial results we are not pursuing this approach at this point in time. PI Nagy plans to meet with Bauer at a meeting in Karlsruhe in March of 1999. She intends to discuss with him in detail his experimental technique to assess whether or not this method is worth trying again.
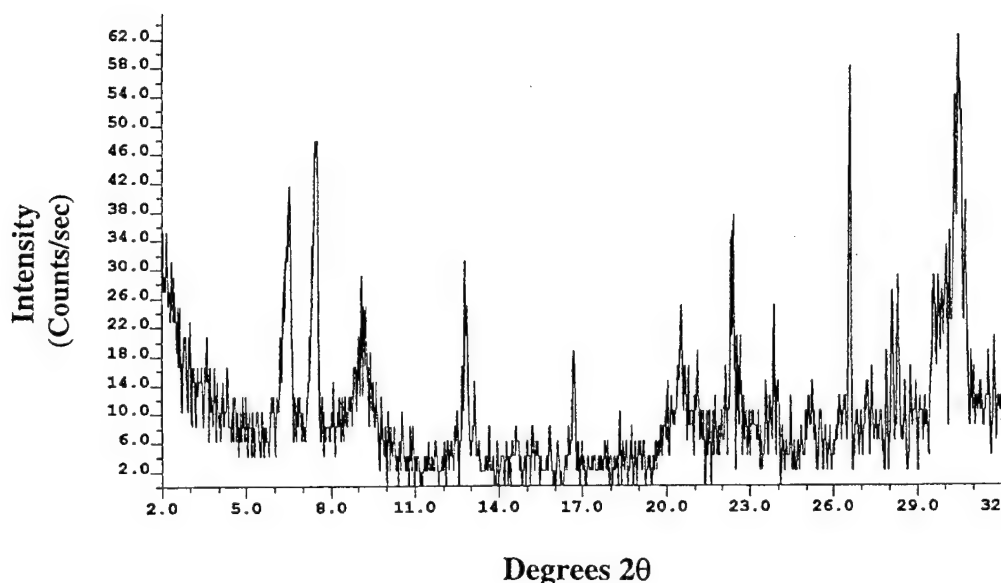

Figure 7: Powder XRD pattern of experiment (d) listed in Table 2. Kaolinite peaks, if present, should occur at 12.36 and 24.87 degrees 2θ. Neither of these peaks is present. The remaining peaks could indicate a mixture of a zeolite, K-feldspar, and possibly a mica.

VI.   Clay Nucleation on Quartz

Summary: A manuscript has been submitted on this research (see Appendix), and is currently in review. This work was conducted in collaboration with Dr. Alain Manceau and coworkers of the

Environmental Geochemistry Group at the University of Grenoble. We have demonstrated that trioctahedral Co-clays nucleate in the surfaces of quartz grains within 6 days at 22°C. This was accomplished using published data obtained by Extended X-ray Absorption Fine Structure (EXAFS) spectroscopy on Co sorption onto quartz, comparison of the spectra with polarized-EXAFS (P-EXAFS) spectroscopy of fine grained clays, our own Co-sorption experiments in which the full solution compositions were determined, and theoretical calculations of clay solubilities.

The results show that clays can nucleate relatively quickly in one of the dominant soil minerals quartz. Acceleration of the process is possible through acid (HCl) washing of the quartz surfaces and sorption of the metal cation in mildly alkaline solutions. These results will be considered when designing the first set of in situ precipitation experiments in the laboratory.

VI.   In-Situ Precipitation Laboratory Experiments

Summary: We have selected two materials for the initial experiments: Min-U-Sil, a micron-sized ground quartz from U. S. Silica, and Dover AFB sediment from the NETTS Dover Test Site. We have obtained about 3 pounds of each of Min-U-Sil 5 (Mill Creek, OK), predominantly 3-10 microns in size, and Min-U-Sil 10 (Pacific, MO), predominantly 5-20 microns in size. We have obtained about 5 pounds of soil from the Dover NETTS Test Site. Both materials are being characterized by XRD for mineralogic composition and by scanning electron microscopy, EDS, and AFM for particle size and particle size distribution.

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APPENDIX OF TECHNICAL PUBLICATIONS

Two technical publications have been prepared to date on the project. The first is a manuscript submitted October 23, 1998 to the journal "American Mineralogist," the journal of the Mineralogical Society of America. This manuscript was written in collaboration with Dr. Alain Manceau at the University of Grenoble and describes spectroscopic and chemical evidence for nucleation of trioctahedral clays in quartz surfaces at room temperature in less than one week. The second is an abstract, presented as a poster at the annual Partners in Environmental Technology Symposium held December 1-3, 1998 in Arlington.

Copies of both publications are contained in the following pages. The abstract is placed before the manuscript.

IN-SITU CLAY FORMATION:
A NEW TECHNOLOGY FOR STABLE CONTAINMENT BARRIERS

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Cost-effective containment barriers must show good chemical and mechanical stability for significant periods of time. Although barrier materials (e.g., colloidal silica and Fe-oxide) that can be precipitated in-situ have been proposed and tested, these materials are not necessarily stable under ambient conditions. During natural lithification of sediments, neoformed clays reduce permeability by nucleating at pore throats. We are synthesizing clay and clay-like materials from aqueous solutions at ambient temperature as the first step in precipitating such materials in situ in soils and sediments. Clays also demonstrate good environmental stability. Clays react relatively slowly in solutions with a wide range of pH, can be tailored to be stable in both arid and humid climates, and can be designed to sorb a range of contaminants.

We synthesized nonexpandable kaolinite clay ($Al_2Si_2O_5(OH)_4$) from solutions containing natural fulvic acid, Si, and Al at 22°C in 42 days. The kaolinite has a maximum grain size of 0.2 microns and shows a sharp X-ray diffraction pattern indicating good crystallinity. In 25 days we synthesized an Al-bearing layered double hydroxide (LDH) ($LiAl_2(OH)_6NO_3 \cdot nH_2O$). LDH solids have structures similar to clays, occur naturally, and have permanent positive charge, making them useful for sorbing anionic contaminants. Al-bearing LDH materials mimic Al-hydroxide phases in having minimum stability in mildly acidic to mildly basic solutions. In 15 days we synthesized mesoaluminosilicate materials, a new class of materials used as catalysts, but also potentially useful as organic contaminant sorbates in the environment. In a related study, we have shown that clays can nucleate on the surfaces of quartz grains, the dominant mineral in most soils and sediments, within six days in the laboratory.